

**REMARKS**

Applicants thank the Examiner for the very thorough consideration given the present application. Claims 1-12 are currently pending in this application. No claims have been amended. Accordingly, no new matter has been added.

In view of the remarks herein, Applicants respectfully request that the Examiner withdraw all outstanding rejections and allow the currently pending claims.

**Issues Under 35 U.S.C. § 103(a)**

Claims 1-12 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over EP 1,172,141 (hereinafter EP '141). Applicants respectfully traverse.

**Claims 1-6**

The Examiner asserts that the claims are rejected “for the reasons set forth in the previous office action”. In response to Applicants’ previous arguments, the Examiner notes that EP ‘141 “adequately suggest[s] the use of all of the claimed elements”.

Applicants respectfully submit that the Examiner has failed to establish a *prima facie* case of obviousness. To establish a *prima facie* case of obviousness, the prior art reference (or references when combined) must teach or suggest all the claim limitations. *In re Vaeck*, 947 F.2d 488, 20 USPQ2d 1438 (Fed. Cir. 1991). Additionally, there must be a reason why one of ordinary skill in the art would modify the reference or combine reference teachings to obtain the invention. A patent composed of several elements is not proved obvious merely by demonstrating that each of its elements was, independently, known in the prior art. *KSR Int’l Co.*

*v. Teleflex Inc.*, 82 USPQ2d 1385 (U.S. 2007). There must be a reason that would have prompted a person of ordinary skill in the relevant field to combine the elements in the way the claimed new invention does. *Id.* The Supreme Court of the United States has recently held that the "teaching, suggestion, motivation test" is a valid test for obviousness, albeit one which cannot be too rigidly applied. *Id.* Rejections on obviousness grounds cannot be sustained by mere conclusory statements; instead, there must be some articulated reasoning with some rational underpinning to support the legal conclusion of obviousness. *Id.*

In the Office Action issued on May 31, 2007, The Examiner asserted that EP '141 inherently meets the presently claimed pH and Raman spectrum of the solution employed for impregnation, as EP '141 discloses an "analogous process for the production of a hydrotreating catalyst". Applicants respectfully disagree.

As to the pH of the carrying solution of Catalyst A in EP '141, experimental data obtained in connection with EP '141 shows that the pH of the carrying solution of Catalyst A prepared in Example 1 of EP '141 is 1.2 (Applicants will be submitting a Declaration Under 37 C.F.R. 1.132 corroborating this data in the near future). In stark contrast, the pH of the carrying solution in the present application is in the range of 2 to 5. Thus, contrary to the Examiner's assertion, the carrying solution of EP '141 does not inherently exhibit the presently claimed pH.

Moreover, the Raman spectroscopy spectrum of the carrying solution of Catalyst A prepared in Example 1 of EP '141 does not have a peak top between  $965\text{ cm}^{-1}$  and  $975\text{ cm}^{-1}$ , as evidenced by the attached graph. In contrast, the carrying solution of the present application has a peak top between  $965\text{ cm}^{-1}$  and  $975\text{ cm}^{-1}$ .

Evidently, the pH and Raman spectroscopy spectrum of the carrying solution of Catalyst A in EP '141 are different from those of the carrying solution of the present application. Thus, the carrying solution of EP '141 does not inherently exhibit the same characteristics of the carrying solution of the instant invention. For this reason alone, the outstanding rejection is improper and should be withdrawn.

In an embodiment of the present invention, the Raman spectroscopy spectrum of the carrying solution has a peak top between  $935\text{ cm}^{-1}$  and  $945\text{ cm}^{-1}$ , and the peak top between  $965\text{ cm}^{-1}$  and  $975\text{ cm}^{-1}$  is higher than the peak top between  $935\text{ cm}^{-1}$  and  $945\text{ cm}^{-1}$  (see, for example, claim 3). Applicants submit that since the carrying solution of Catalyst A in EP '141 does not have any peak top between  $965\text{ cm}^{-1}$  and  $975\text{ cm}^{-1}$ , EP '141 can not possibly teach or suggest that the peak top between  $965\text{ cm}^{-1}$  and  $975\text{ cm}^{-1}$  is higher than the peak top between  $935\text{ cm}^{-1}$  and  $945\text{ cm}^{-1}$ .

Additionally, EP '141 does not teach the use of molybdenum, phosphorus, cobalt and nickel in the carrying solution, as presently claimed. For instance, all of the Examples of EP '141 (paragraphs [0025]–[0031]) utilize carrying solutions comprising only molybdenum, cobalt and phosphorous, but not nickel.

Applicants have discovered that superior and unexpected results are obtained by utilizing a carrying solution containing molybdenum, phosphorous, cobalt and nickel. The Examiner's attention is respectfully directed to the enclosed technical paper entitled "*Inhibition Effect of Hydrogen Sulfide and Ammonia on NiMo/Al<sub>2</sub>O<sub>3</sub>, CoMo/Al<sub>2</sub>O<sub>3</sub>, NiCoMo/Al<sub>2</sub>O<sub>3</sub> Catalysts in Hydrosulfurization of Dibenzothiophene and 4, 6-Dimethyldibenzothiophene*", published in the Journal of the Japan Petroleum Institute, 48(5), pp. 281-289. In this paper, the Applicants

describe the results of experiments comparing the performance of Co/Mo/Ni/P, Co/Mo/P and Mo/Ni/P catalysts. As evidenced by this paper, a Co/Mo/Ni/P catalyst (as recited in claim 1) exhibits superior performance over a Co/Mo/P catalyst, as that disclosed by EP '141 (*see* Tables 1A and 1B, as well as Section 2.1: Catalyst Preparation).

Moreover, catalysts A to F of EP '141 are used for hydrotreating Middle East direct distillation gas oil (see paragraph [0032]), rather than for hydrotreating a vacuum gas oil distillate product, as recited in present claim 1.

#### Claims 7-12

Claims 7-12 are allowable at least for the reasons set forth above. Furthermore, these claims are further distinguishable from the cited reference for the following reasons.

Claim 7 and dependent claims thereof are directed to a method for producing a hydrotreating catalyst by bringing a carrying solution into contact with a carrier, wherein the hydrotreating catalyst contains molybdenum, phosphorus, cobalt and nickel, and does not contain inorganic or organic acids other than phosphoric acid.

The Examiner states that "[w]ith respect to the new claims excluding an acid other than phosphoric acid, it is considered that such is embraced by the teaching of EP 1,172,141". Applicants respectfully disagree, and submit that the Examiner has not fulfilled his burden of establishing that it would have been *prima facie* obvious to modify EP '141 by excluding citric acid.

Excluding citric acid from the solution of EP '141 would render the solution of EP '141 unsatisfactory for its intended purpose. For instance, at [0005], this reference discloses that "the

inventor has discovered that when an organic acid, such as citric acid, etc., and hydrogen peroxide are further added to a supporting liquid containing a metal belonging to group VIB of the Periodic table and phosphorous, a catalyst with excellent desulfurization activity can be prepared". Thus, EP '141 teaches that citric acid and hydrogen peroxide are essential components of the hydrotreating catalyst (see also claim 1 of EP '141). If these components are excluded from the supporting liquid, it is clear from the disclosure of EP '141 that the invention of EP '141 would not work (see Table 1 of EP '141). Applicants respectfully submit that modifying EP '141 by eliminating citric acid would result in an undesirable carrying solution that would not exhibit an acceptable level of desulfurization activity, thus being unsatisfactory for its intended purpose.

Furthermore, the Examiner is respectfully reminded that the omission of an element and retention of its function is an indicia of unobviousness (*see* MPEP 2144.04). As disclosed at page 3, lines 17-23 of the present Specification, the present inventors have been able to develop a solution that exhibits excellent desulfurization activity (retention of function) without the addition of citric or other organic acids (omission of a step).

Since EP '141 relates to a carrying solution in which citric acid and hydrogen peroxide are essential components, the Examiner's assertion that EP '141 teaches the exclusion of acids other than phosphoric acid is incorrect. Contrary to the Examiner's assertion, excluding an acid other than phosphoric acid is not "embraced by the teaching of EP 1,172,141".

Because the invention, as set forth in Applicants' claims, is not disclosed or made obvious by the cited prior art, reconsideration and withdrawal of this rejection are respectfully requested.

**Conclusion**

All of the stated grounds of rejection have been properly traversed, accommodated, or rendered moot. Applicants therefore respectfully request that the Examiner reconsider all presently outstanding rejections and objections and that they be withdrawn. It is believed that a full and complete response has been made to the outstanding Office Action and, as such, the present application is in condition for allowance.

Should there be any outstanding matters that need to be resolved in the present application, the Examiner is respectfully requested to contact Marc S. Weiner, Reg. No. 32,181 at the telephone number of the undersigned below, to conduct an interview in an effort to expedite prosecution in connection with the present application.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37.C.F.R. §§1.16 or 1.14; particularly, extension of time fees.

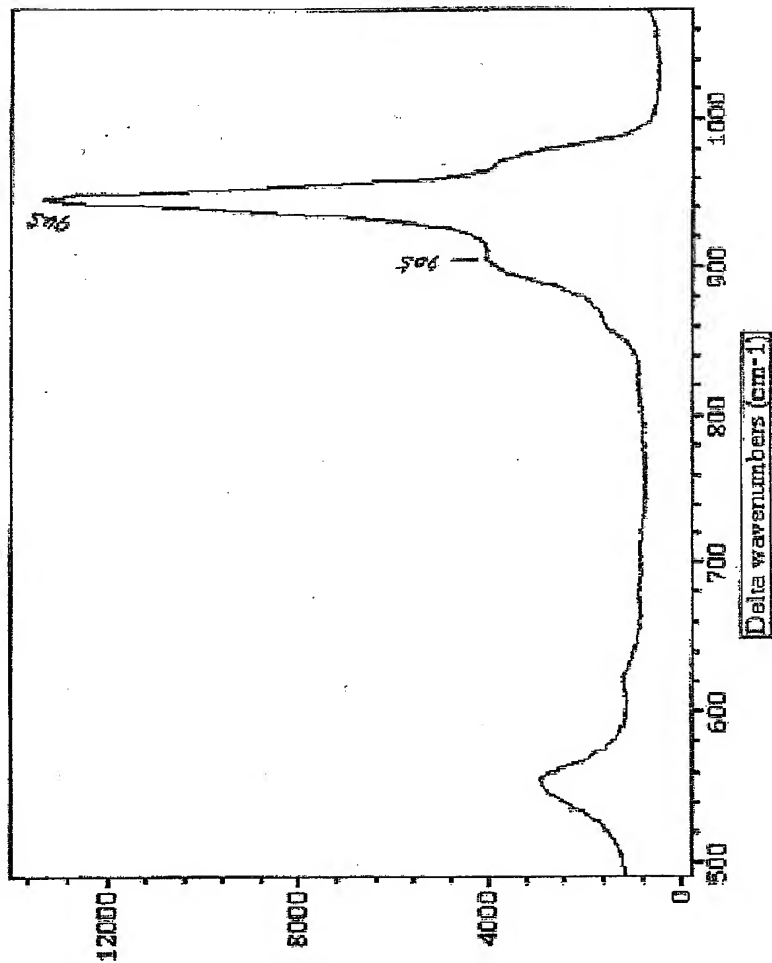
Dated: **MAR 31 2008**

Respectfully submitted,

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Raman spectroscopy spectrum of Catalyst A prepared in Example 1 of EP 1,172,141



## [Regular Paper]

Inhibition Effect of Hydrogen Sulfide and Ammonia on NiMo/Al<sub>2</sub>O<sub>3</sub>, CoMo/Al<sub>2</sub>O<sub>3</sub>, NiCoMo/Al<sub>2</sub>O<sub>3</sub> Catalysts in Hydrodesulfurization of Dibenzothiophene and 4,6-Dimethyldibenzothiophene

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Model hydrodesulfurization catalysts (Co<sub>2</sub>.75Mo<sub>1.1</sub>, Ni<sub>2</sub>.75Mo<sub>1.1</sub> and Ni<sub>0.9</sub>Co<sub>1.85</sub>Mo<sub>1.1</sub> wt%/γ-Al<sub>2</sub>O<sub>3</sub>) prepared by impregnation of similar supports with similar starting materials were used in the following test reactions: hydrodesulfurization (HDS) of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene, with and without addition of H<sub>2</sub>S or NH<sub>3</sub>. The presence of H<sub>2</sub>S or NH<sub>3</sub> has a profound effect on the catalyst ranking and the activities of various reaction pathways, e.g., the hydrogenation (HYD) route and the direct desulfurization (DDS) route. In the case of the HDS of DBT and 4,6-DMDBT, hydrogen sulfide only weakly poisoned CoMo and NiCoMo catalyst, whereas a NiMo catalyst is poisoned more strongly. On the other hand, ammonia strongly poisoned HYD route of CoMo catalyst, whereas DDS route of NiMo catalyst is not at all poisoned in the case of the HDS of DBT. The trimetallic NiCoMo catalyst exhibited the best performance in the conversion of DBT. A comparison of the HYD and DDS rate constants among CoMo, NiMo and NiCoMo catalysts shows that in the presence of rich H<sub>2</sub>S, the activity of HYD and DDS of the NiCoMo catalyst equals the sum of the activity of the HYD of NiMo catalyst and of the DDS of CoMo catalyst. On the other hand, in the presence of rich NH<sub>3</sub>, the activity of the NiCoMo catalyst equals the sum of the HYD and DDS of NiMo catalyst, which each in turn are higher than those of CoMo catalyst. This dual promoting effect of NiCoMo catalyst causes higher activity than either NiMo or CoMo catalyst in the presence of either rich H<sub>2</sub>S or rich NH<sub>3</sub>.

**Keywords**

Hydrodesulfurization, Inhibition effect, Nickel molybdenum catalyst, Cobalt molybdenum catalyst, Hydrogen sulfide, Ammonia

**1. Introduction**

The development of more active catalysts for more efficient hydrotreating processes is important in view of upcoming oil regulations. Further tightening of diesel fuel sulfur restrictions has been proposed and will be implemented worldwide in the near future. In order to reduce particulate matter and NO<sub>x</sub> emission from diesel-fueled vehicles, the maximum permissible sulfur content of diesel fuel will be 50 wt ppm by the end of the year 2004 in Japan. Requirement of substantially "sulfur free" diesel fuel (10 wt ppm or less) has been proposed for the future. The European Commission proposed a mandatory "zero sulfur" restriction (10 wt ppm or less) from 2011. Japan is also considering requiring "sulfur free" diesel fuel by 2007. Therefore, much attention is given to effective technological solutions for ultra-low sulfur diesel fuel, particularly sulfur-

free diesel fuel production. In deep hydrodesulfurization (HDS), employed to accomplish this goal, the most refractory sulfur compounds in gas oil are alkyl-dibenzothiophenes with alkyl groups near the sulfur atom (in positions 4 and 6)<sup>1,2)</sup>. The other problem is inhibition by H<sub>2</sub>S<sup>3,4)</sup> and nitrogen compounds including NH<sub>3</sub><sup>5,6)</sup>. These inhibitors are generated during HDS and HDN reactions and their concentration is higher under the conditions of deep HDS.

Two solutions for ultra-low sulfur diesel fuel production have been developed by the authors. A simple solution known as the "CoMo/NiMo Catalyst Relay" system was described in ref.7. This solution can achieve 50 wt ppm sulfur production without major revamp of conventional deep HDS units. In this system, the first part of the catalyst bed is the CoMo type, which is the pretreatment catalyst for ultra deep HDS, arranged over the main NiMo catalyst which is the second part. The main function of the CoMo catalyst is to achieve HDS of reactive sulfur compounds such as dibenzothiophene (DBT). The NiMo catalyst in the

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second bed is the main catalyst for ultra-low sulfur diesel fuel production and achieves HDS of refractory sulfur compounds such as 4,6-dimethyldibenzothiophene (4,6-DMDBT), even in the presence of high concentrations of catalyst poisoning materials such as hydrogen sulfide and ammonia.

A more effective solution is a two-stage process with gas/liquid separation (GLSP) in the middle of the unit<sup>6</sup>. This process has a great potential for producing sulfur-free diesel fuel production ( $S = 10$  wt ppm or less). Removal of produced  $H_2S$  and  $NH_3$  in the middle of the unit accelerates HDS in the second-stage reactor here described. Typical straight gas oil derived from Middle East heavy oil contains 1.2 wt% of sulfur and 100–300 wt ppm of nitrogen compounds. During ultra-deep HDS, in the first-stage reactor most of the nitrogen compounds are converted to  $NH_3$ , and some 1.0% of sulfur compounds is converted to  $H_2S$ . The authors will examine the inhibition effect of these substances on ultra-deep HDS in the second-stage reactor.

We have also developed a new HDS catalyst, using the promotion effect of both Ni and Co<sup>9</sup>. The activity of the catalyst on HDS and HDN is higher than that of conventional NiMo and CoMo catalysts in a limited range of Ni/Co ratio,  $0.5 < Co/(Co + Ni) < 0.75$ .

In this work, this promoter effect was examined in more detail, special attention being paid to the inhibition of  $NH_3$  and  $H_2S$ . The Ni-, Co- and NiCo-promoted Mo catalysts were prepared by pore-volume impregnation, each in a similar support. In this way, we were able to clearly understand the inhibition of  $NH_3$  and  $H_2S$  on the HDS catalysts in conversion of DBT and 4,6-DMDBT.

## 2. Experimental

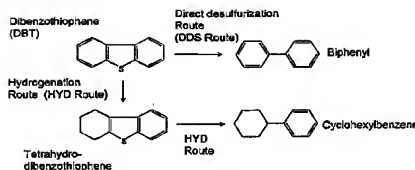
### 2.1. Catalyst Preparation

Catalysts were prepared by successive incipient wetness impregnations of  $\gamma-Al_2O_3$  (pore volume:  $0.78 \text{ cm}^3 \cdot \text{g}^{-1}$ , specific surface area:  $380 \text{ m}^2 \cdot \text{g}^{-1}$ ) with an aqueous solution of  $MoO_3$  and Ni carbonate or Co carbonate and with an aqueous solution of phosphoric acid. The catalysts contained 11 wt% Mo and 2.75 wt% Co or 2.75 wt% Ni, or 1.85 wt% Co + 0.9 wt% Ni.

After the impregnation, each catalyst was dried in an oven at 393 K for 15 h and finally calcined at 773 K for 30 min. The catalysts were crushed and sieved to the desired particle size before use. A sample of 0.5 g of a catalyst was diluted with  $9 \text{ cm}^3$   $\alpha-Al_2O_3$  to achieve continuous up-flow in a fixed bed reactor, thereby preventing incomplete catalyst wetting and bypass flow.

### 2.2. Model Feed Experiments

The model feed consisted of a solution of either 0.20 wt% of 4,6-DMDBT (Acros Organics, purity > 95%) which contains 300 wt ppm sulfur, or 0.58 wt% DBT (Kanto Chemical Co., Inc., purity > 98%) which con-



Scheme 1 Reaction Scheme for HDS Reaction of DBT (from ref. 10)

tains 1000 wt ppm sulfur, in a decaline solution. The amount of the sulfur compounds referred to here is that measured in the inlet of the second-stage reactor in our two stage process incorporating gas/liquid separation. The effect of  $H_2S$  on the catalyst performance was tested by addition of 0.05 wt% of a hydrogen sulfide-generating compound (dimethyldisulfide, DMDS, Kanto Chemical Co., Inc., purity > 99%, sulfur amount corresponding to 10,000 wt ppm of  $H_2S$ ). To explore the effect of  $NH_3$  on the catalyst activity in the HDS of 4,6-DMDBT and DBT, 0.13 wt% of a  $NH_3$ -generating compound (tri-*n*-butyl amine, TBA, Kanto Chemical Co., Inc., purity > 99%, sulfur amount corresponding to 300 wt ppm of  $NH_3$ ) was added to the reactant mixture. The mixed catalysts  $(Co(2.75)Mo(11)/Ni(2.75)Mo(11)/Ni(0.9)Co(1.85)Mo(11)/\gamma-Al_2O_3)$ , amount in parentheses after a metal is wt%—hereafter the same) were pre-sulfided *in-situ* with a decaline solution of 2 wt% DMDS at 5.0 MPa and 573 K for 8 h.

The catalysts were tested at 563–603 K at a total pressure of 5.0 MPa, weight hourly space velocity of  $30 \text{ h}^{-1}$ , under  $6 \text{ l} \cdot \text{h}^{-1}$  hydrogen flow for 4,6-DMDBT reactions.

For the reactions of DBT, the catalysts were tested at 583–623 K at a total pressure of 5.0 MPa, weight hourly space velocity of  $60 \text{ h}^{-1}$  under  $6 \text{ l} \cdot \text{h}^{-1}$  hydrogen flow.

### 2.3. Catalyst Activity and Reaction Pathways

The reaction products were quantitatively analyzed by gas chromatography with a Shimadzu GC-17A equipped with a 60 m WCOT fused silica capillary column, a CP-Sil 8 CB column (VARIAN, 0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness), and a flame ionization detector (FID) and also identified by GC-MS (Shimadzu 17A/QP-5000) and GC-SCD (Sulfur chemiluminescent detector, ANTEK7090 with FID-GC, Shimadzu GC2010). On the other hand, the result of sulfur stripping of the product oil was checked by XRF (X-ray fluorescence ZSX101c, RIKEN) to correct the FID results.

All the HDS activities are characterized by their first order reaction rate ( $k_{HDS}$ ) for DBT or 4,6-DMDBT.

The HDS of DBT proceeds through two different parallel pathways<sup>10</sup> (Scheme 1): the so-called direct desulfurization pathway (DDS), where a direct C–S bond cleavage of the DBT molecule leads to production

of biphenyl (BP), or the hydrogenation pathway (HYD), which yields cyclohexylbenzene (CHB) by an initial hydrogenation of one of the aromatic rings of the DBT followed by C-S bond cleavage.

The HYD and the DDS selectivity are based on the product concentration ratio  $((\text{CHB})/(\text{BP} + \text{CHB}))$  and  $(\text{BP}/(\text{BP} + \text{CHB}))$ , respectively. The HDS of 4,6-DMDBT proceeds through similar pathways (Scheme 2)<sup>(1)</sup>. In the 4,6-DMDBT case, the DDS pathway leads to production of 3,3'-biphenyl (BPs) and the HYD pathway leads to 3,3'-dimethylcyclohexylbenzene (CHBs) and 3,3'-dimethylbicyclohexyl (BCHs).

In this case, the HYD and the DDS selectivity are based on the product concentration ratio  $(\text{CHBs} + \text{BCHs})/(\text{BPs} + \text{CHBs} + \text{BCHs})$  and  $(\text{BPs}/(\text{BPs} + \text{CHBs} + \text{BCHs}))$ , respectively.

It should be noted that an intermediate primary hydrogenated product, like tetrahydrodibenzothiophenes (THDBTs), and an intermediate secondary hydrogenated product, like hexahydrodibenzothiophenes (HHDBTs), are formed along the HYD pathway. These concentrations are very low and are not detected in the most

cases, and therefore, they were omitted in the calculation of the conversion or selectivity.

We estimated the first order reaction rate constant for the conversion of DBT or 4,6-DMDBT ( $k_{\text{HDS}}$ ) is the summation of the first order reaction rate constant for the DDS route ( $k_{\text{D}}$ ) and the first order reaction rate constant for the HYD route ( $k_{\text{H}}$ ),  $k_{\text{D}}$  and  $k_{\text{H}}$  being defined as follows,

$$k_{\text{D}} = (\text{HYD selectivity}) \times k_{\text{HDS}} \quad (1)$$

$$k_{\text{H}} = (\text{DDS selectivity}) \times k_{\text{HDS}} \quad (2)$$

$$k_{\text{HDS}} = k_{\text{D}} + k_{\text{H}} \quad (3)$$

### 3. Results

#### 3.1. Model Feed Experiments with 4,6-DMDBT

The first order overall reaction rate constants of the different catalysts for the conversion of 4,6-DMDBT with and without additives are shown in Table 1A.

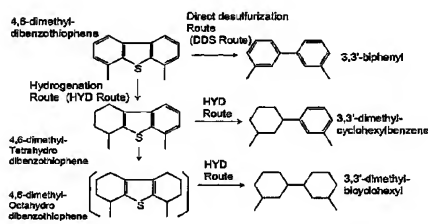
NiMo is by far the most active catalyst in the blank test. The ratio of the first order reaction rate constant of NiMo to that of the blank test at the same temperature strongly decreases. The first order reaction rates of other catalysts also decrease in the presence of H<sub>2</sub>S. The apparent activation energy of CoMo catalysts is lower than the other catalysts (Table 2).

The presence of NH<sub>3</sub> significantly decreases the overall reaction rate constant for the conversion of 4,6-DMDBT for all tested catalysts to a greater extent than that for the blank test. Interestingly, the reaction rate constant of CoMo catalyst significantly decreases with addition of NH<sub>3</sub>. The apparent activation energy of NiMo is lower than the other catalysts (Table 2).

#### 3.2. Model Feed Experiments with DBT

The first order overall reaction rate constants of the different catalysts for the conversion of DBT with and without additives are shown in Table 1B.

The rate constant of NiCoMo catalyst in the blank



Scheme 2 Reaction Scheme for HDS Reaction of 4,6-DMDBT (from ref. 11)

Table 1A The First Order Rate Constants of the Conversion for 4,6-DMDBT

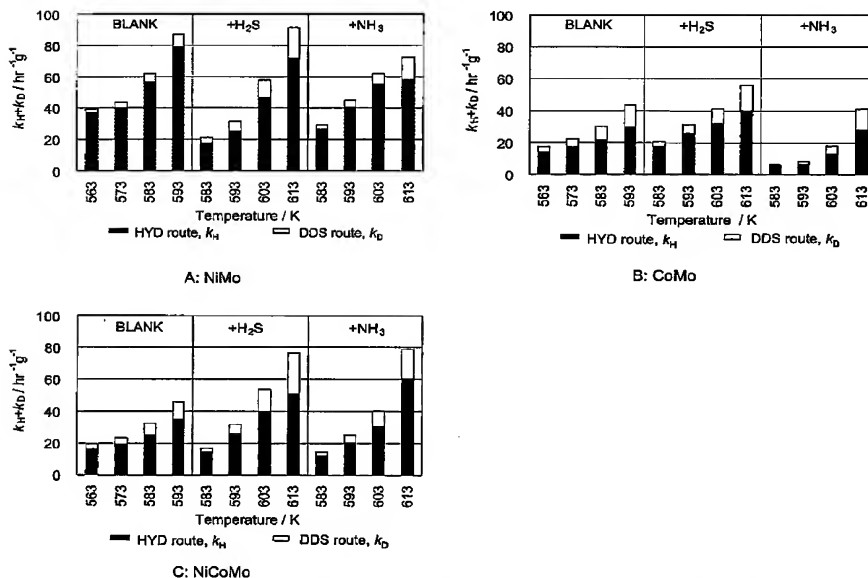
Temperature	Blank				Addition of H <sub>2</sub> S (+H <sub>2</sub> S)				Addition of NH <sub>3</sub> (+NH <sub>3</sub> )			
	563 K	573 K	583 K	593 K	583 K	593 K	603 K	613 K	583 K	593 K	603 K	613 K
NiCoMo	19.1	23.0	32.4	46.1	16.6	31.8	53.8	76.4	14.7	25.1	40.1	79.2
NiMo	39.1	43.3	61.5	86.6	21.0	31.2	57.6	90.9	29.0	44.8	61.5	72.0
CoMo	17.5	22.6	30.4	43.9	20.6	31.3	41.2	56.3	6.6	8.4	18.1	40.9

Table 1B The First Order Rate Constants of the Conversion for DBT

Temperature	Blank				Addition of H <sub>2</sub> S (+H <sub>2</sub> S)				Addition of NH <sub>3</sub> (+NH <sub>3</sub> )			
	583 K	593 K	603 K	613 K	593 K	603 K	613 K	623 K	593 K	603 K	613 K	623 K
NiCoMo	82.9	104.6	121.2	141.4	47.0	74.8	108.8	152.5	65.5	90.2	132.2	178.0
NiMo	66.7	87.2	104.8	125.2	25.9	40.7	59.2	78.4	73.0	98.8	139.6	152.3
CoMo	58.1	86.6	109.8	129.5	44.8	66.6	85.4	93.6	50.1	82.4	106.1	120.5

Table 2 Apparent Activation Energy for HDS of 4,6-DMDBT and DBT  
[kcal · mol<sup>-1</sup>]

Catalyst	4,6-DMDBT			DBT		
	NiMo	NiCoMo	CoMo	NiMo	NiCoMo	CoMo
Blank test	17.8	19.7	20.0	14.5	12.1	18.5
+H <sub>2</sub> S	35.0	35.7	23.1	26.9	28.2	17.9
+NH <sub>3</sub>	21.4	38.3	43.7	18.5	24.4	21.0



$k_H$  (black bar), the first order reaction rate constant for HYD route;  $k_D$  (white bar), the first order reaction rate constant for DDS route;  $k_{\text{HDS}} = k_H + k_D$ . A: NiMo, B: CoMo, C: NiCoMo.

Fig. 1 The First Order Reaction Rate Constant for the Conversion of 4,6-DMDBT

test is slightly higher than those of the other catalysts, the rate constants of the catalysts being the almost the same.

The presence of H<sub>2</sub>S significantly decreases the overall reaction rate constant for the conversion of DBT for all tested catalysts to a greater extent than that for the blank test (Table 1B). NiCoMo is the most active catalyst for the conversion of DBT in the presence of H<sub>2</sub>S. The apparent activation energy of CoMo is lower than those of the other catalysts (Table 2).

The presence of NH<sub>3</sub> significantly decreases the activity of CoMo; the rates of the NiMo and NiCoMo

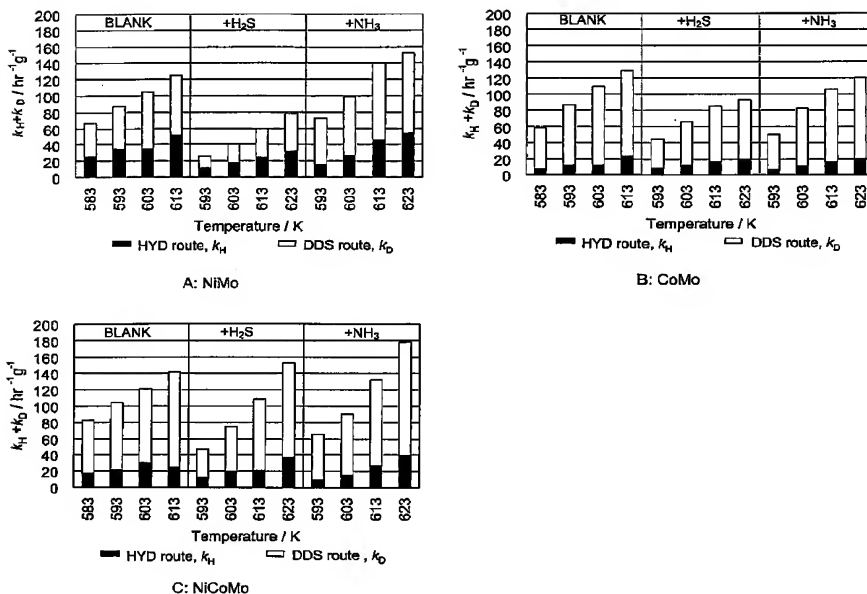
catalyst are not decreased by NH<sub>3</sub> as much.

### 3.3. Reaction Pathway

The first order reaction rate constants for the conversion of 4,6-DMDBT and DBT were calculated separately for the HYD route ( $k_H$ ) and for the DDS route ( $k_D$ ).

The rate constant divided into  $k_H$  and  $k_D$  components for each catalyst for the conversion of 4,6-DMDBT are shown in Figs. 1A-1C. The HYD route ( $k_H$ ) is dominant in all the test results of 4,6-DMDBT.

The  $k_H$  and  $k_D$  of each catalyst for the conversion of DBT are shown in Figs. 2A-2C. The DDS route is



$k_H$  (black bar), HYD activity;  $k_D$  (white bar), DDS activity;  $k_{HDS} = k_H + k_D$ . A: NiMo, B: CoMo, C: NiCoMo.

Fig. 2 The First Order Reaction Rate Constant for the Conversion of DBT

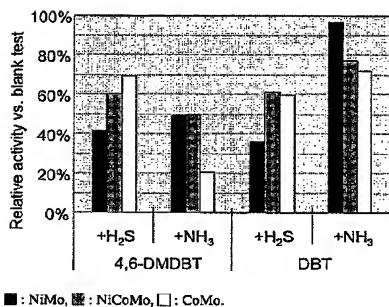


Fig. 3 The Average Inhibition Degree of the Activity for the Conversion of 4,6-DMDBT and DBT against Each Blank Test at the Same Temperature in the Presence of  $H_2S$  and  $NH_3$

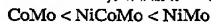
dominant in all the test results of DBT. The HYD selectivity of NiMo and NiCoMo catalysts is higher than that of CoMo.

We observed the differences resulting from different routes among the catalysts, and found that the degree of inhibition by  $H_2S$  and  $NH_3$  are differ according to the route. The reason for these differences will be discussed in the following section.

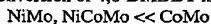
### 3. 4. Inhibition Effect of $H_2S$ and $NH_3$

Each first order reaction rate constant is compared to the rate constant of the blank test at the same temperature. The average of the activity relative to the blank test is shown as relative activity in Fig. 3.

The ranking of the inhibition effect of  $H_2S$  on the conversion of 4,6-DMDBT is as follows,

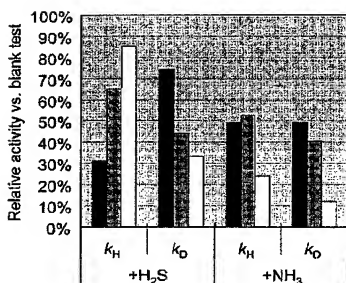


The ranking of the inhibition effect of  $NH_3$  on the conversion of 4,6-DMDBT is as follows,



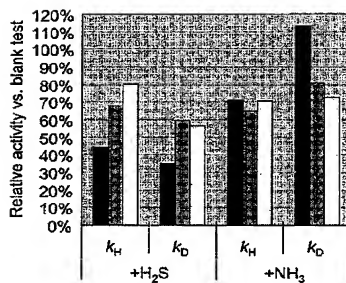
The ranking of the inhibition effect of  $H_2S$  on the conversion of DBT is as follows,





■: NiMo, ▨: NiCoMo, □: CoMo.

Fig. 4 The Average Inhibition Degree of  $k_H$  and  $k_D$  for the Conversion of 4,6-DMDBT against Each Blank Test at the Same Temperature in the Presence of H<sub>2</sub>S and NH<sub>3</sub>



■: NiMo, ▨: NiCoMo, □: CoMo.

Fig. 5 The Average Inhibition Degree of  $k_H$  and  $k_D$  for the Conversion of DBT against Each Blank Test at the Same Temperature in the Presence of H<sub>2</sub>S and NH<sub>3</sub>

The ranking of the inhibition effect of NH<sub>3</sub> on the conversion of DBT is as follows,

NiMo < NiCoMo < CoMo

#### 4. Discussion

##### 4.1. Inhibition Effect of H<sub>2</sub>S and NH<sub>3</sub> on HYD and DDS Reaction Pathways

To identify the active site of each promoted catalyst, we estimated which route was poisoned by H<sub>2</sub>S and NH<sub>3</sub> by comparing separately  $k_H$  and  $k_D$  activity of the blank test with the tests using H<sub>2</sub>S- and NH<sub>3</sub>-containing feeds.

Figure 4 shows the average inhibition degree of  $k_H$  and  $k_D$  for the conversion of 4,6-DMDBT, against each blank test at the same temperature in the presence of H<sub>2</sub>S and in the presence of NH<sub>3</sub>.

The inhibition of H<sub>2</sub>S in the HYD route on NiMo catalyst is clearly shown. CoMo catalyst is weakly poisoned by H<sub>2</sub>S. NiCoMo poisoning is moderate, between NiMo and CoMo.

On the other hand, direct desulfurization route of CoMo and NiCoMo are strongly poisoned by H<sub>2</sub>S. This implies H<sub>2</sub>S is adsorbed on the active site of DDS.

The inhibition effect of H<sub>2</sub>S and NH<sub>3</sub> is more clearly shown in the conversion of 4,6-DMDBT than in the conversion of DBT. The sulfur atom in 4,6-DMDBT is difficult to remove because of the steric hindrance of the methyl groups<sup>12</sup>. The reaction route for HDS of 4,6-DMDBT is usually HYD; therefore, this cause of the difference in inhibition has clearer effect than in the reaction route for HDS of DBT.

The inhibition effect of H<sub>2</sub>S on each catalyst in the HDS of DBT is shown in Fig. 5.

The role of H<sub>2</sub>S on hydrotreating sulfide catalysts

has been studied extensively in the literature<sup>2)~4)</sup>. In general, by adsorption of H<sub>2</sub>S, DDS active sites may be converted into HYD active sites, which can change the rate of elementary reaction steps<sup>13)</sup>. Texier *et al.*<sup>14)</sup> reported that the addition of H<sub>2</sub>S increases hydrodesulfurization activity. Reinhoudt *et al.*<sup>5)</sup> also reported that the addition of DMDS, which means H<sub>2</sub>S addition, increases CoMo catalyst activity of HDS for 4,6-alkylated DBT and DBT. In our study, we did not observe such an increase; however, the high tolerance to H<sub>2</sub>S poisoning of NiCoMo and CoMo has the same mechanism as this increase in activity. The adsorption of H<sub>2</sub>S on the CoMo catalyst surface may form a HYD active site.

Raybaud *et al.*<sup>15)</sup> reported the most stable Co-promoted MoS<sub>2</sub> (1010) surfaces, found using *ab initio* quantum chemical calculation. The study shows that Co atoms are apt to be substituted for Mo atoms on the MoS<sub>2</sub> (1010) edge and the most stable surface is not covered at all by sulfur and presents only four-fold coordinated Co atoms. There are many coordinatively unsaturated (CUS) sites where a sulfur atom can adsorb are located on the most stable Co-promoted MoS<sub>2</sub> surface.

Travert *et al.*<sup>16)</sup> also reported the most stable CoMo and NiMo catalyst surfaces under actual working conditions, calculating the adsorption energy of hydrogen using the same calculation program as Raybaud *et al.*<sup>15)</sup> and considering the thermodynamic equilibrium of these surfaces with H<sub>2</sub>S and H<sub>2</sub> in the gas phase. The results show that hydrogen is easily dissociated on CoMo catalyst surfaces of the Co-S-Co bridge site which is one of the most stable Co-promoted MoS<sub>2</sub> surfaces under actual working conditions, while hydrogen breaks Ni-S bonds on the NiMo catalyst surface edge of the S-Ni-S

Table 3 Comparison of  $k_H$  and  $k_D$  for the Conversion of 4,6-DMDBT or DBT between the Proportional Distribution and the NiCoMo Catalyst ( $k_H$ ;  $\text{h}^{-1} \cdot \text{g}^{-1}$ ,  $k_D$ ;  $\text{h}^{-1} \cdot \text{g}^{-1}$ )

Feed	Reaction temperature [K]	CoMo		NiMo		NiCoMo		Proportional distribution <sup>a)</sup>	
		$k_H$	$k_D$	$k_H$	$k_D$	$k_H$	$k_D$	$k_H$	$k_D$
Blank test	583	8		41	17	66	14	47	
	593	13		52	22	83	20	66	
	603	12		70	30	91	20	88	
+H <sub>2</sub> S	593	9		14	12	35	10	29	
	603	13		23	19	55	14	43	
	613	17		34	21	88	20	57	
+NH <sub>3</sub>	593	7	44		9	56	10	48	
	603	12	71		15	75	17	71	
	613	16	90		28	110	26	91	

a) The proportional distribution of 66%CoMo and 33%NiMo.

Mesh: Higher  $k_H$  and  $k_D$  values between CoMo and NiMo.

bridge structure.

The CUS site is a DDS active site, and after the adsorption of S atom on the CUS site, a Co-S-Co bridge structure is formed on the Co-promoted MoS<sub>2</sub> (1010) surface. This Co-S-Co bridge structure activates hydrogen<sup>16)</sup> and likely influences the HYD active site.

The inhibition effect of NH<sub>3</sub> is shown in Figs. 4 and 5. NH<sub>3</sub> poisoned strongly both the HYD and DDS active site on CoMo catalyst in the case both of DBT and 4,6-DMDBT. In the case of 4,6-DBT poisoned with NH<sub>3</sub>, NiCoMo catalyst behaves like NiMo catalyst. In the case of DBT poisoned with NH<sub>3</sub>, NiMo catalyst shows a high tolerance for NH<sub>3</sub>. Especially,  $k_D$  of NiMo catalyst exhibits almost the same activity as the blank test in the case of DBT poisoned with NH<sub>3</sub>.

#### 4.2. The Activity of NiMo Catalyst

NiMo catalyst causes the highest level of HDS conversion of 4,6-DMDBT blank test. Among our experimental conditions, this is the case where H<sub>2</sub>S concentration is the lowest. An ideal gas/liquid separation system with high HDS-promoting catalyst in the first-stage reactor realizes such a lean H<sub>2</sub>S condition. Hensen *et al.*<sup>17)</sup> also reported high activity of NiMo catalyst under lean H<sub>2</sub>S conditions.

The NiMo catalyst has a high tolerance for NH<sub>3</sub>. Figure 5 shows that the HYD active site on NiMo catalyst is poisoned by NH<sub>3</sub> as are the other catalysts; however, the DDS active site on NiMo catalyst is not poisoned at all. This phenomenon suggests that the DDS active site on NiMo catalyst has a high tolerance for NH<sub>3</sub>.

#### 4.3. The Activity of CoMo Catalyst

The CoMo catalyst is not as active as the other two catalysts except under H<sub>2</sub>S rich conditions. However, H<sub>2</sub>S rich conditions are the most typical actual conditions for HDS of straight-run gas oil, and therefore CoMo catalyst is commonly used for actual HDS of

straight-run gas oil. The activity of CoMo catalyst is strongly poisoned by NH<sub>3</sub>. Reinhoudt *et al.*<sup>9)</sup> also reported the poisoning effect of carbazole on CoMo catalyst in the case of 4,6-alkylated DBT. If the feed contains a lot of nitrogen compounds, CoMo catalyst is not suitable for HDS.

#### 4.4. The Activity of NiCoMo Catalyst

NiCoMo catalyst is the best catalyst for DBT conversion in all cases. After calculating HYD and DDS activity, we found an interesting result in the summation of  $k_H$  and  $k_D$ .

NiCoMo catalyst comprises Ni, Co and Mo impregnated in the same support. On this surface, there are two active sites located together. Examining the inhibition effect of H<sub>2</sub>S and NH<sub>3</sub>, we found that the nature of NiMo catalyst and of CoMo catalyst are quite different from each other. CoMo catalyst has a high tolerance for H<sub>2</sub>S and NiMo catalyst has a high tolerance for NH<sub>3</sub>. If there are two different active sites on NiCoMo catalyst, and  $k_H$  and  $k_D$  are different for NiMo and CoMo, the NiCoMo HDS activity should be the summation of higher values of  $k_H$  and  $k_D$ .

We list the higher of the values of  $k_H$  and  $k_D$  for NiMo and for CoMo, and compare the calculated values of NiCoMo catalyst in Table 3.

Although there are some variations at higher temperatures, the activity of NiCoMo catalyst is the summation of the higher values of  $k_H$  and  $k_D$  for NiMo and for CoMo in the presence of rich H<sub>2</sub>S and NH<sub>3</sub> conditions.

The CoMo catalyst has a higher  $k_D$  value than the NiMo catalyst while the NiMo catalyst has a higher value of  $k_H$ . NiCoMo catalyst activity is a summation of  $k_D$  of CoMo and  $k_H$  of NiMo; therefore the total HDS activity is higher than either or CoMo. It is known that catalytic reactions proceed through the lowest barrier. NiCoMo catalyst has two kinds of active sites, and the reaction pathway proceeds through the active site with the lower barrier. Thus, NiCoMo catalyst

activity is the sum of the higher values of  $k_H$  and  $k_D$  for CoMo and for NiMo.

The variation of  $k_H$  among catalysts in the presence of  $NH_3$  is larger than in the presence of  $H_2S$ . As shown in Table 3, the HYD route of all catalysts is poisoned by  $NH_3$ . If we find the proportion of CoMo and NiMo and incorporate this in calculations, the estimated HYD activity of NiCoMo is much more accurate. This implies that the HYD active sites are poisoned by  $NH_3$ .

If the NiCoMo catalyst is just a mixture of NiMo and CoMo catalyst, the activity should be the proportional distribution of NiMo and CoMo activity. The NiCoMo catalyst comprising 1.9 wt% Co and 0.85 wt% Ni is loaded on an  $Al_2O_3$  support. Co and Ni atoms are intended to substitute for atoms at the  $MoS_2$  edge surface<sup>19</sup>, and for this reason the NiCoMo catalyst surface is 1/3 NiMo and 2/3 CoMo.

We compared the  $k_H$  and  $k_D$  calculated based on the proportion of NiMo and CoMo catalyst with the actual  $k_H$  and  $k_D$  of NiCoMo catalyst. Table 3 also shows a comparison between  $k_H$  and  $k_D$  for the conversion of 4,6-DMDBT or DBT computed from the proportional distribution and those of the actual NiCoMo catalyst. The  $k_H$  and  $k_D$  value of NiCoMo catalyst is higher than those calculated from the proportional distribution between NiMo and CoMo except in the case of the blank test of HDS for 4,6-DMDBT. The blank test for the conversion of 4,6-DMDBT (300 wt ppm as S atoms) generates very low  $H_2S$  concentration. The other cases generate conditions rich in  $H_2S$  or  $NH_3$ , and therefore NiCoMo catalyst shows higher activity than the proportional distribution would indicate. These results imply the NiCoMo catalyst causes high activity of both HYD and DDS in the presence of rich  $H_2S$  or  $NH_3$  conditions.

Finally, we determined the best combination for the two-stage process with gas/liquid separation as follows. NiCoMo catalyst is the best catalyst for the first-stage reactor because NiCoMo has the high tolerance for both  $H_2S$  and  $NH_3$ . NiMo catalyst is the best catalyst for the second-stage reactor because NiMo has high HDS activity under lean  $H_2S$  conditions.

## 5. Conclusion

It was demonstrated that the presence of  $H_2S$  and  $NH_3$  has a large effect on the catalyst ranking and relative importance of reaction pathways, i.e. the activity of HYD route ( $k_H$ ) and the activity of DDS route ( $k_D$ ), of various catalysts for the conversion of both DBT and 4,6-DMDBT.

In the presence of  $H_2S$ , NiCoMo catalyst is the best catalyst for the conversion of DBT. We examined the HYD and DDS activity of NiCoMo, and found that the NiCoMo catalyst activity is the sum of the higher of the

HYD values for NiMo and CoMo, and the higher of the DDS values for NiMo and CoMo. This implies the dual promoting effect of Ni and Co on NiCoMo catalyst.

The best combination of catalysts in the first-stage and second-stage reactor for the two-stage process with gas/liquid separation is considered to be as follows.

In the first-stage reactor, NiCoMo catalyst is the best catalyst because of the high tolerance for both  $H_2S$  and  $NH_3$ . In the second-stage reactor, NiMo catalyst is the best catalyst because of the high HDS activity under lean  $H_2S$  conditions. Among industrial hydrotreating catalysts, a NiW catalyst would be an alternative for a NiMo catalyst because NiW catalyst is well known its high hydrogenation activity in lean  $H_2S$  conditions.

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## 要 旨

ジベンゾチオフェンおよび4,6-ジメチルジベンゾチオフェンの脱硫反応におけるNiMo/Al<sub>2</sub>O<sub>3</sub>、CoMo/Al<sub>2</sub>O<sub>3</sub>、NiCoMo/Al<sub>2</sub>O<sub>3</sub>触媒への硫化水素とアンモニアの阻害効果

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出発原料、担体、担持方法の影響の少ないモデル触媒 (Co2.75Mo11, Ni2.75Mo11およびNi0.9Co1.85Mo11 wt %/γ-Al<sub>2</sub>O<sub>3</sub>) を調製して、4,6-ジメチルジベンゾチオフェンとジベンゾチオフェンの脱硫反応におけるH<sub>2</sub>S、NH<sub>3</sub>の影響を検討した。脱硫反応で考えられている水素化脱硫および直接脱硫ルートごとの性能をNiMo、CoMo、NiCoMo触媒と比較した。その結果、CoMo触媒とNiCoMo触媒はH<sub>2</sub>Sに対する被毒の影響が少なかったのに対して、H<sub>2</sub>SはNiMo触媒の両反応ルートの活性を大きく低下させた。一方、CoMo触媒の水素化脱硫ルートが

NH<sub>3</sub>により強く被毒されるが、NiMo触媒の直接脱硫ルートはNH<sub>3</sub>に被毒されないことを明らかにした。また、NiCoMo触媒に関しては、NiMoとCoMoの担持比率から計算される水素化および直接脱硫ルートの反応速度定数の比例配分値より高い性能を示し、その値はNiMo触媒、CoMo触媒の各反応ルートのより高い値の和に近い値を示すことが分かり、被毒物質のある雰囲気ではNiMo単独あるいはCoMo単独より高い活性を示すことを明らかにした。

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